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 雰囲気酸素分圧制御下におけるトレランス因子と六方晶
 LnMnO_3 相の生成の関係

 Relationship between Oxygen Partial Pressure and
 Tolerance Factor in the Formation of Hexagonal LnMnO_3
 Phase

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1. Introduction

The equilibrium crystal structure of LnMnO_3 (Ln: Lanthanide) is orthorhombic ($o\text{-LnMnO}_3$, space group: $Pbnm$) when La^{3+} to Dy^{3+} are used as Ln^{3+} , and hexagonal ($h\text{-LnMnO}_3$, space group: $P6_3cm$) when Ho^{3+} to Lu^{3+} are used as Ln^{3+} ¹. Nevertheless, it is reported that the $h\text{-LnMnO}_3$ phase forms even in the DyMnO_3 system when oxygen partial pressure of atmospheric gas (P_{O_2}) is decreased during the solidification from the melt.² Although the formation of $h\text{-LnMnO}_3$ phase in DyMnO_3 system is reported to be attributed to oxygen deficiency, the details still remain unclear.

The structural stability of LnMnO_3 can be evaluated by the following tolerance factors, TF ³.

$$TF = \frac{r_{\text{Ln}} + r_{\text{O}}}{\sqrt{2}(r_{\text{Mn}} + r_{\text{O}})} \quad (1)$$

where r_{Ln} , r_{O} , and r_{Mn} are the ionic radii of Ln^{3+} , O^{2-} , and Mn^{3+} , respectively. In LnFeO_3 , $TF < 0.87$ is reported to be the criterion for the formation of $h\text{-LnFeO}_3$ ⁴. It is assumed that LnMnO_3 can be characterized as the same as LnFeO_3 because the ionic radii of Fe^{3+} and Mn^{3+} are the same. When Ho^{3+} to Lu^{3+} with relatively small ionic radii are used as Ln^{3+} so that the $h\text{-LnMnO}_3$ phase is formed as the stable phase, corresponding the TF is calculated at $TF < 0.85$. Note that if the ionic radius of Mn can be increased, it is mathematically possible to satisfy the $TF < 0.85$ with relatively large Ln^{3+} , as can be seen from Eq. (1). Since oxygen deficiency is expected in the LnMnO_3 melt under low P_{O_2} , Mn^{3+} may be reduced into Mn^{2+} to maintain electrical neutrality. In this case, the calculated TF would be decreased because the ionic radius of Mn^{2+} is larger than that of Mn^{3+} .

In the present study, DyMnO_3 melt was solidified at various P_{O_2} condition to examine whether oxygen deficiency was induced. The purpose of this study was to investigate whether the decrease in TF corresponding to oxygen deficiency facilitates the formation of $h\text{-LnMnO}_3$ as same as that corresponding to decrease in r_{Ln} .

2. Experimental procedure

Dy_2O_3 and Mn_2O_3 powders, mixed in an agate mortar, were melted on a copper hearth by irradiation from

a semiconductor laser and then solidified into a spherical DyMnO₃ sample with a diameter of 2 mm. The spherical sample was heated to approximately 2300 K to completely melt it and then solidified in an aerodynamic levitation furnace (ADL) using a mixture of Ar and O₂ gases. Temperature and solidification process of the sample was monitored by a monochromatic pyrometer and a high-speed video camera (HSV), respectively. The solidified samples were analyzed by powder x-ray diffractometer (XRD), and thermogravimetric differential thermal analysis (TG-DTA) at $P_{O_2} = 1 \times 10^5$ Pa.

3. Results and discussion

Figure 1 shows typical TGA curves for DyMnO₃ samples solidified at $P_{O_2} = 1 \times 10^5$ Pa and 1 Pa. The mass of DyMnO₃ samples increases with elevating the temperature up to 1200 K and changes little at the subsequent cooling stage. This confirms the oxygen deficiency in the as-solidified DyMnO₃ sample. The increase in the sample mass becomes large in the sample solidified at $P_{O_2} = 1$ Pa, indicating that the oxygen deficiency is enhanced by decreasing the P_{O_2} .

When the oxygen deficiency is induced in the DyMnO₃ sample depending on the P_{O_2} , the following chemical reaction, being possible together with reduction of Mn³⁺ into Mn²⁺, should be considered.



$$\Delta G^\circ = -534400 + 224 T \text{ [J}\cdot\text{mol}^{-1}]^5 \quad (3)$$

When assuming that the increase in sample mass is due to the supply of oxygen corresponding to the oxygen deficiency and Mn²⁺ corresponding to the oxygen deficiency is allocated to MnO and DyMnO_{3+δ} phases, the amount of Mn²⁺ would be evaluated from the production ratio of MnO and *h*-DyMnO₃ phases. Figure 2 shows XRD profiles of DyMnO₃ samples solidified at various P_{O_2} together with the calculated *TF* from the above assumptions. When calculated *TF* corresponding to oxygen deficiency is 0.844 under P_{O_2} of 1×10^5 Pa, the diffraction peaks for *h*-DyMnO₃ (□) and *o*-DyMnO₃ (Δ) phases are detected in the XRD profile of the sample.

However, the diffraction peaks for *o*-LnMnO₃ phase disappears when calculated *TF* corresponding to oxygen deficiency decreases to 0.836 under P_{O_2} of 3×10^3 Pa. This indicates that decrease in *TF* corresponding to oxygen deficiency facilitates the formation of *h*-DyMnO₃.

Further decrease in the calculated *TF* corresponding to oxygen deficiency under lower P_{O_2} enhances the formation of cubic MnO (*c*-MnO, space group: *Fm3-m*) (○) and cubic Dy₂O₃ (*c*-Dy₂O₃, space group: *la-3*) (◇) together with those of *h*-LnMnO₃. This is evidence that the chemical reaction of Eq. (2) follows when decreasing P_{O_2} .

4. Summary

DyMnO₃ samples were solidified at various P_{O_2} condition. As a result, the decrease in P_{O_2} results in oxygen deficiency in as-solidified samples. Formation of *h*-DyMnO₃ was promoted by decreasing *TF* corresponding to oxygen deficiency.

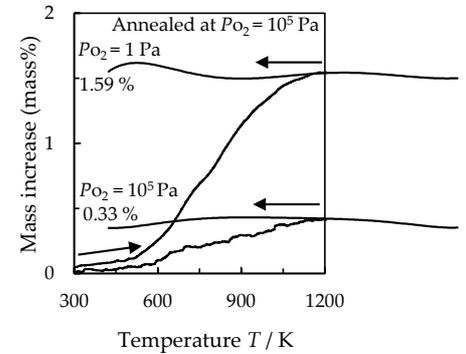


Fig. 1. TGA curves for DyMnO₃ samples solidified at $P_{O_2} = 1 \times 10^5$ Pa and 1 Pa. Annealed at $P_{O_2} = 10^5$ Pa

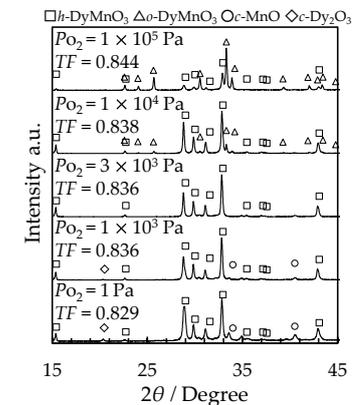


Fig. 2. X-ray diffraction patterns of DyMnO₃ samples solidified at various P_{O_2} .

Reference

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